DENITROGENATION OF MODEL OIL USING IMIDAZALIUM-BASED IONIC LIQUID

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ABSTRACT

Removal of aromatic nitrogen contaminants from petroleum is important for many reasons. First, their combustion leads directly to the formation of nitrogen oxides (NOx); emissions of NOx, which contributes to acid rain, are under increasingly stringent control by environmental regulation. This thesis contains the study of Model Oil (iso-octane) by extraction with imidazalium-based ionic liquid. The objective of this experiment is to determine the nitrogen compound (Pyridine) removal efficiency of imidazalium-based ionic liquid (3-ethylimidazalium-ethyl phosphate) from iso-octane. In order to characterize the imidazalium based ionic liquids, the process of characterization of 3-ethylimidazalium-ethyl phosphate was conducted by using Fourier Transform Infra Red (FTIR) spectroscopy.

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LIST OF ABBREVIATIONS

C4	Butane
NOx	Nitrogen oxides
HPLC	High Performance Liquid Chromatography
FTIR	Fourier Transform Infrared
MALDI-TOF	Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry
GC	Gas Chromatography
IR	Infrared
C	Carbon
H	Hydrogen
N	Nitrogen
IL	Ionic liquid
S	Sulphur
wt-ratio	weight ratio
ppm	part pe million
M1V1	concentration 1×volume 1

1.0 INTRODUCTION

1.1 Motivation and statement of problem

Developments in the field of separation of pollutants, such as nitrogen and sulphur-containing compounds in the refinery industry have been experiencing a rapid growth due to more and stricter environmental protection regulations on the release of these pollutants from transportation fuels. Ionic liquids on the other hand are potential alternative solvents for the separation of aromatic hydrocarbons (benzene, toluene, ethyl benzene) from C4 to C10 aliphatic hydrocarbon mixtures. The prospect of ionic liquids as alternative solvents to substitute less desirable organic media is under intensive research. The low vapor pressure and ability to adjust the physical and chemical properties of ionic liquids by selection of the cations and anions, makes them attractive for a wide range of applications. For example, ionic liquid have already illustrated their potential as alternative solvents and reaction media. Furthermore, ionic liquids have been applied in solvent extraction processes and in gas separations (Ikenna Anugwom *et al.* 2011).

In fuels, nitrogen compounds act as precursors for nitrogen oxides (NO_X) which are environmental pollutants. Nitrogen are responsible for the formation of smog, sour gases, acid rain and NOx emissions, these nitrogen compounds needs to be removed. Ionic liquid can be used to absorbed nitrogen compounds from fuels. Therefore, in this study is to investigate the capability of imidazalium-based ionic liquid in removing nitrogen compound from fuel.

1.2 Objectives

The following are the objectives of this research:

- To investigate the potential of imidazalium-based ionic liquids in removing nitrogen compound from fuel.

1.3 Scope of Study

The following are the scope of this research:

i) To characterize the synthesized ionic liquids, 3-Ethylimidazalium-Ethyl Phosphate.
ii) To study the removal performance of nitrogen compound from Iso-Octane.

1.4 Main contribution of this work

This experiment main purpose is to find the right imidazalium-based ionic liquid that will remove the some percentage of nitrogen compound from fuel. This experiment use 3-ethylimidazalium-ethyl phosphate, we will test with the fuel that contain nitrogen compound. The percentage of the decrease or increase amount of nitrogen in the mixture will be check by refer to HPLC result. From the graph we get from HPLC data results,we can know the outcome of this experiment.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of review about ionic liquid characteristic and its usage. Also review about the function of FTIR and HPLC spectroscopy. Previous work for denitrogenation also state in this chapter. Use imidazalium-based ionic liquid too. The figure of the result also being show in the previous denitrogenation experiment.

Chapter 3 gives a review of materials and methods use for this experiment. Material use are by borrow from the chemical lab store. Methods involve are caharacterization of ionic liquid, preparation of standard sample, preparation of sample of model oil + pyridine + ionic liquid, hplc spectroscopy and preparation of mobile phase. Chemicals use in this experiment are iso-octane, pyridine, 3-ethylimidazalium-ethyl phosphate and methanol.

Chapter 4 is review about Denitrogenation of model oil. This chapter focus on the results of this experiment. Consist of results of FTIR spectroscopy spectroscopy. Also contain the possible structure of 3-ethylimidazalium-ethyl phosphate and the table of wavelength and their respective molecular motion and functional group.

Chapter 5 give a review about conclusion of the experiment base on the result get in the chapter four. Consist of conclusion and future work recommendation step to make the experiment more succesful and accurate.

2.0 LITERATURE REVIEW

2.1 *Overview*

Ionic Liquid is a salt that are poorly coordinated, which cause it become liquid if temperature is below 100°C or even at room temperature. If at least an ionic liquid contain one ion that has delocalized charge and organic- can prevents formation of a stable crystal lattice to ionic liquid. ionic liquid , example 1-ethyl-3-methylimidazolium ethylsulphate-melting point <20 °C. Inorganic salt like sodium chloride have melting point at 801 °C. Instead of melting point a glass transition is observed especially if long aliphatic side chains are involved. Special characteristics of ionic liquid: thermal stability, low vapor pressure, electric conductivity, interesting solvent properties, liquid crystalline structures, high electroelasticity, high heat capacity and non flammability. Applications of ionic liquid: for lubricants and additive, use for lubricants and fuel additives, for electroelastic material, use for artificial muscles and robotics, for analytics, use for MALDI-TOF-matrices, GC-head-space-solvents and protein crystallization, for liquid crystals, use for displays, for heat storage, use for thermal, for solvents, use for Bio-catalysis, organic reaction and catalysis, Nano particles synthesis and polymerization, fluids for electrolytes, use for fuel cells, sensors, batteries, supercaps, metal finishing and coating, for separation, use for gas separations, extractive distillation, extraction and membranes. (ALDRICH, 2005)

2.2 Introduction

This paper present the result of the FTIR spectroscopy. From FTIR result, they are show the graph of different wavelength for different element. The element for each wavelength can be refer by table of IR Absorptions for Representative Functional Groups. This table contains info about group of alkanes, alkenes, alkynes, aromatics, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, acid chlorides, anhydrides, amines, amides, alkyl halides, nitriles, isocyanates, isothiocyanates, imines, nitro groups, mercaptans, sulfoxides, sulfones, sulfonates, phosphines and phosphine oxides. This table shows the molecular motion (etc: C-H strecth, =CH strecth) and wavenumber in unit of cm^{-1}.

2.3 *Previous Work on Denitrogenation*

Liquid-liquid extraction by using 1-ethyl-3-methylimidazolium chloride [C2 mim] [Cl] was found to be a very promising method for the removal of N- and S-compounds. This was evaluated by using a model oil (dodecane) with indole as a neutral nitrogen compound and pyridine as a basic nitrogen compound. An extraction capacity of up to 90 wt% was achieved for the model oil containing pyridine. The presence of aromatic compounds in the model oil decreases the extraction capacity of the ionic liquid. The presence of an aromatic compound in the sample affected the extraction capacity of the ionic liquid probably due to the fact that the ionic liquid exhibits a high affinity towards the aromatics. The effect of the ionic liquid-to-oil ratio was investigated in the extraction of N-compounds from the model oil. The extraction capacity improved as the ratio of IL-to-oil was increased, for indole Figure 1 and pyridine Figure 2, respectively. The extraction capacity also improved with an increase in the IL to oil ratio.

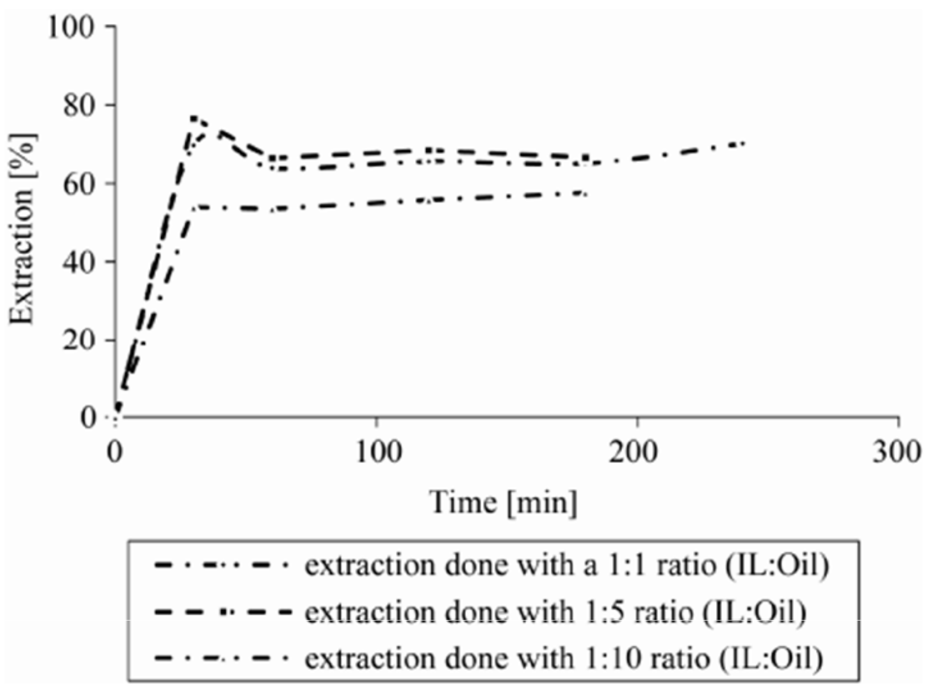

Figure 2-1: Extraction of the model oil containing indole as the N-compound with IL ([C2 mim] [Cl]) at 60°C.

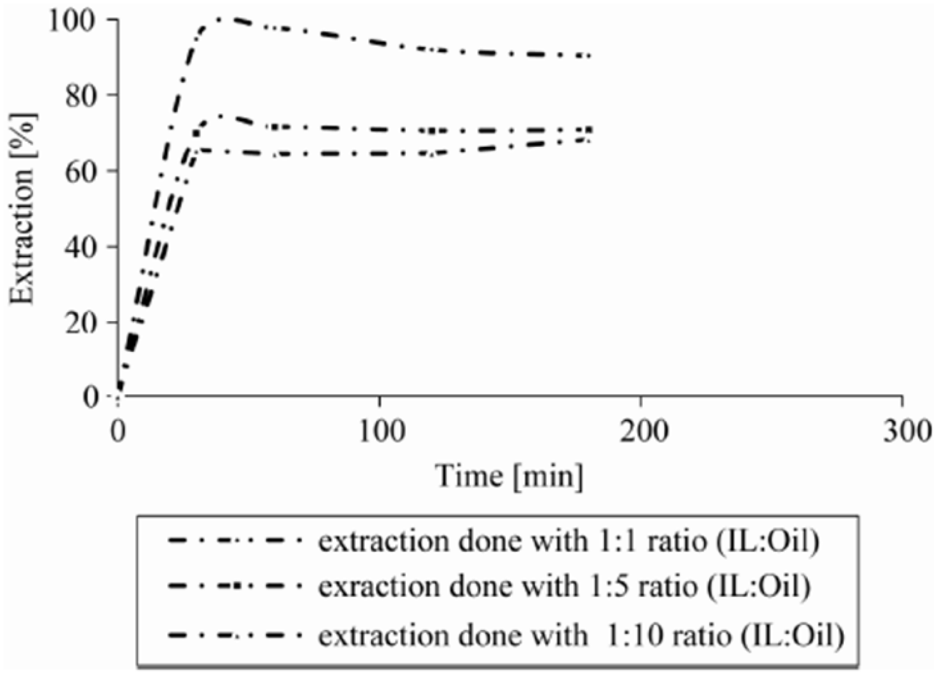

Figure 2-2: Extraction of the model oil containing pyridine as the N-compound with IL ([C2 mim] [Cl]) at 60°C.

The model oil in the current study was a mixture containing 3000 ppm of the nitrogen compound (indole or pyridine) in dodecane. Different ionic liquid to oil ratios were selected 1:1, 1:5, 1:10 (wt-ratio) and the extraction conditions were allowed to be the same in all cases: temperature was 60°C while 15 min mixing contact time between the oil and IL was used (Figures 1 and 2). The extraction of the model oil containing indole as the nitrogen compound was performed at 60°C and the IL-to oil ratio (wt) was 1:5. In equilibrium, 70% of the nitrogen compound was removed (Figure 1). In the case of a 1:1 IL-to-oil ratio 76% of indole was removed in equilibrium at 60°C. This is an indication that a higher IL-to-oil ratio does not improve the extraction effectiveness prominently. Moreover, thinking about potential large-scale process, 1:5 IL to oil ratio is already rather high.

2.4 Summary

Ionic Liquid is a salt that are poorly coordinated, which cause it become liquid if temperature is below 100°C or even at room temperature. Applications of ionic liquid: for lubricants and additive, for electroelastic material, for analytics, for liquid crystals, for solvents, fluids for electrolytes and for gas separations. FTIR shows the elemental group occur in the ionic liquid use and HPLC shows whether the pyridine (nitrogen) is reduce or not from the graph that have been conctructed. From the theory it looks like extraction capacity improved as the ratio of IL-to-oil was increased but from the previous experiment result a higher IL-to-oil ratio does not improve the extraction effectiveness prominently.

3.0 MATERIALS AND METHODS

3.1 Overview

The 3-ethylimidazalium-ethyl phosphate is analyze by the FTIR spectroscopy to know the elemental group occur in that ionic liquid.

3.2 Introduction

3.2.1 Characterization of Ionic Liquid

Some sample of the 3-ethylimidazalium was put on the sample plate in the FTIR equipment. Close the cover of the place of the sample plate. From the computer click start button to begin the simulation. As the graph of wavelength occur, the data was save in the compact disk for futher analysis later. The analysis of the wavelength data can be done by refer table of IR Absorptions for Representative Functional Groups. The functional group and molecular motion were found based on the table of IR Absorptions for Representative Functional Groups.

3.2.2 Preparation of standard sample

The pyridine needed to be add to the 100mL of model oil to get 1500ppm was calculated by using formula:

$$1500 \qquad = \frac{}{0.1}$$

Conversion: density = mass/volume

Volume pyridine = mass pyridine/density pyridine

The 100mL mixture was divided into two container for each container contain 50mL. One of the 50mL mixture was used to make concetration of 1000ppm, 800ppm, 500ppm and 250ppm while the other one 50mL mixture is save. By using formula $M_1V_1 = M_2V_2$, the V_2 needed was got to produce 1000ppm, 800ppm, 500ppm and 250ppm concentration of model oil mixture by assume V_1 for some value. V_2 is the total volume needed to produce wanted concentration model oil mixture by adding it with 1500ppm model oil mixture for amount of V_1 we assumed earlier. V_2-V_1 is equal to volume needed more from 1500ppm model oil mixture to produce certain concentration. After all the standard sample are prepared, five sample from the five different concentration were made. All preparation of sample into vial bottles must be made by using filter to avoid any the failure of the HPLC equipment.

3.2.3 Preparation of sample of model oil + pyridine + ionic liquid

From sample prepared in the schott bottle 50mL, take volume needed to produce 1(ionic liquid):1(model oil mixture) ratio sample. Assume for 1 : 0.5mL. Prepare for one sample for ratio 1:1 for each concentration. The step 1 to 2 are repeated for the ratio of 1:4. After all the sample are prepared, the sample are place in the vials bottle by using syringe and filter.

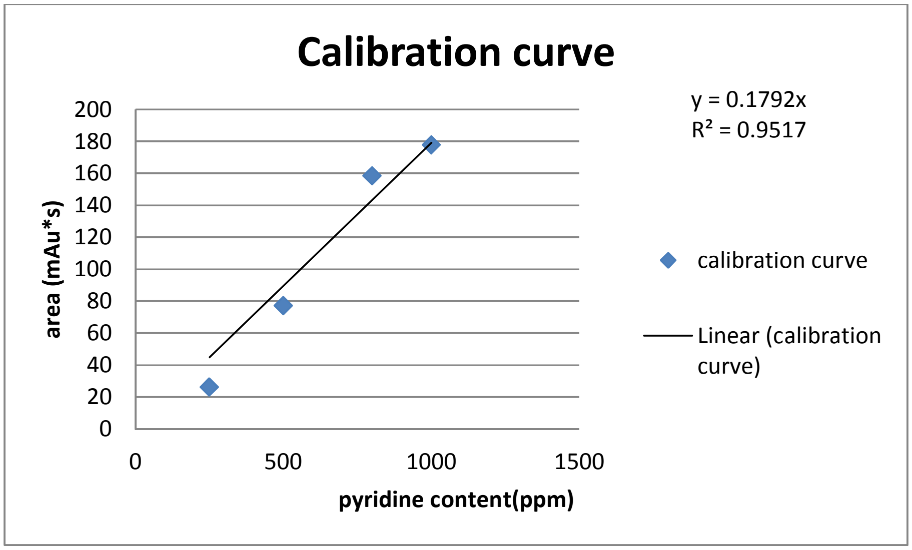

Figure 3-1: Calibration curve from HPLC results.

3.2.4 HPLC Spectroscopy

Ten sample were placed in the place of the vials bottle. They were placed according to the name starting from four sample of standard sample, four sample of ratio 1:1 and four sample of ratio 1:4. The HPLC spectroscopy equipment was run by lab coordinator. The results of the analysis of the ten sample were got after 24 hours of analysis.

3.2.5 Preparation of mobile phase

Mobile phase for this experiment was methanol. In the ratio of 1:9, 90% percent of methanol was used to produce the solution of mobile phase while other 10% ratio for ultra pure water. For produce 1 liter mobile phase, 100mL of utlra pure water was added into 900mL of methanol. The mobile phase solution was filtered by using membrane filter. Then the mobile phase solution was degas with sonicator.

3.3 Chemicals

3.3.1 Model oil

The model oil use for this experiment was iso-octane. It is flammable in liquid and vapor state. It can causes causes eye, skin, and respiratory tract irritation. Its vapors may cause drowsiness and dizziness. Can cause aspiration hazard if swallowed as it can enter lungs and cause damage. It is very toxic to aquatic organisms as it may cause long-term adverse effects in the aquatic environment. For handling, only use it under a chemical fume hood togehter with explosion-proof equipment. The user should wear personal protective equipment. It should keep away from open flames, hot surfaces and sources of ignition. For storage of iso-octane, it must keep away from open flames, hot surfaces and sources of ignition. The containers of iso-octane must tightly closed in a dry, cool and well-ventilated place.

3.3.2 Pyridine

Pyridine was used as source of nitrogen in this experiment. It is flammable in liquid and vapor state. Its vapor may cause flash fire. If inhale it can cause irritation, headache, drowsiness, dizziness and loss of coordination for short term exposure and for long term exposure can cause nausea, vomiting, diarrhea, stomach pain, loss of appetite, dizziness, sleep disturbances, emotional disturbances, loss of coordination and nerve damage. If the effects still occur, the victim should move to uncontaminated area. If breathing is difficult, oxygen should be administered by qualified personnel. The victims should get immediate medical attention.

3.3.3 3-Ethylimidazalium-ethyl phosphate

Ionic liquid use for this experiment was 3-ethylimidazalium-ethyl phosphate. It is corrosive to skin, eyes, and respiratory system. Its liquid or spray mist may produce tissue damage, particularly in mucous membranes of the eyes, mouth and respiratory tract. If contact to the skin may produce burns. If contact to the eyes can result in corneal damage or blindness. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. It is a corrosive materials that may cause serious injury if ingested. If contact to the eyes occur, remove any contact lenses. Flush eyes with running water for a minimum of 15 minutes, occasionally lifting the upper and lower eyelids. If the chemical gets spilled on a clothed portion of the body, remove the contaminated clothes as quickly as possible and protecting your own hands and body. Place the victim under a deluge shower. If the chemical touches the victim's exposed skin, such as the hands: Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap.

3.3.4 Methanol

A mobile phase used in the HPLC equipment is methanol. It should not use in a confined area without proper ventilation. If wear the contact lenses it may cause further damage in case of splash into eye. It should avoid use near heat, flames, sparks, and other sources of ignition. It is extremely flammable in liquid and vapour state. It is fatal if swallowed. It may damage fertility or the unborn child (fetotoxic and teratogenic effects), cause damage to eyes and central nervous system if ingested or inhaled. If contact with eye, remove contact lenses if worn. In case of contact, immediately flush eyes with plenty of clean running water for at least 15 minutes, lifting the upper and lower eyelids occasionally. If contact with skin, remove contaminated clothing. In a shower, wash affected areas with soap and water for at least 15 minutes. Seek medical attention if irritation occurs or persists. Wash clothing before reuse.

3.4 Summary

In order to know the percent of reduce nitrogen compound in the model oil it is needed to prepared standard sample and two different ratio of ionic liquid + model oil mixture. From the standard sample it will become the references to know wether the nitrogen removal was succeeded or not. The step involve for this experiment were characterization of ionic liquid by FTIR spectroscopy, preparation for different concentration of ionic liquid, preparation of some sample of different ratio and the analysis of the samples wtih HPLC spectroscopy. This experiment was done by using the model oil,pyridine and ionic liquid.

4.0 Denitrogenation of Model Oil

4.1Overview

This chapter review about the results of this thesis. The result get from the FTIR spectroscopy analysis. Result of FTIR analysis show the graph of different wavelength for different element. Its analyze the element wavelength in range of 700cm^{-1} to 4000cm^{-1}. The lowest wavelength is 748.11cm^{-1} which refer to aromatics, C-H bend (ortho) and the highest wavelength is 3391.50cm^{-1} which refer to alcohols, O-H stretch.

4.2 *Introduction*

4.2.1 Results of FTIR spectroscopy analysis

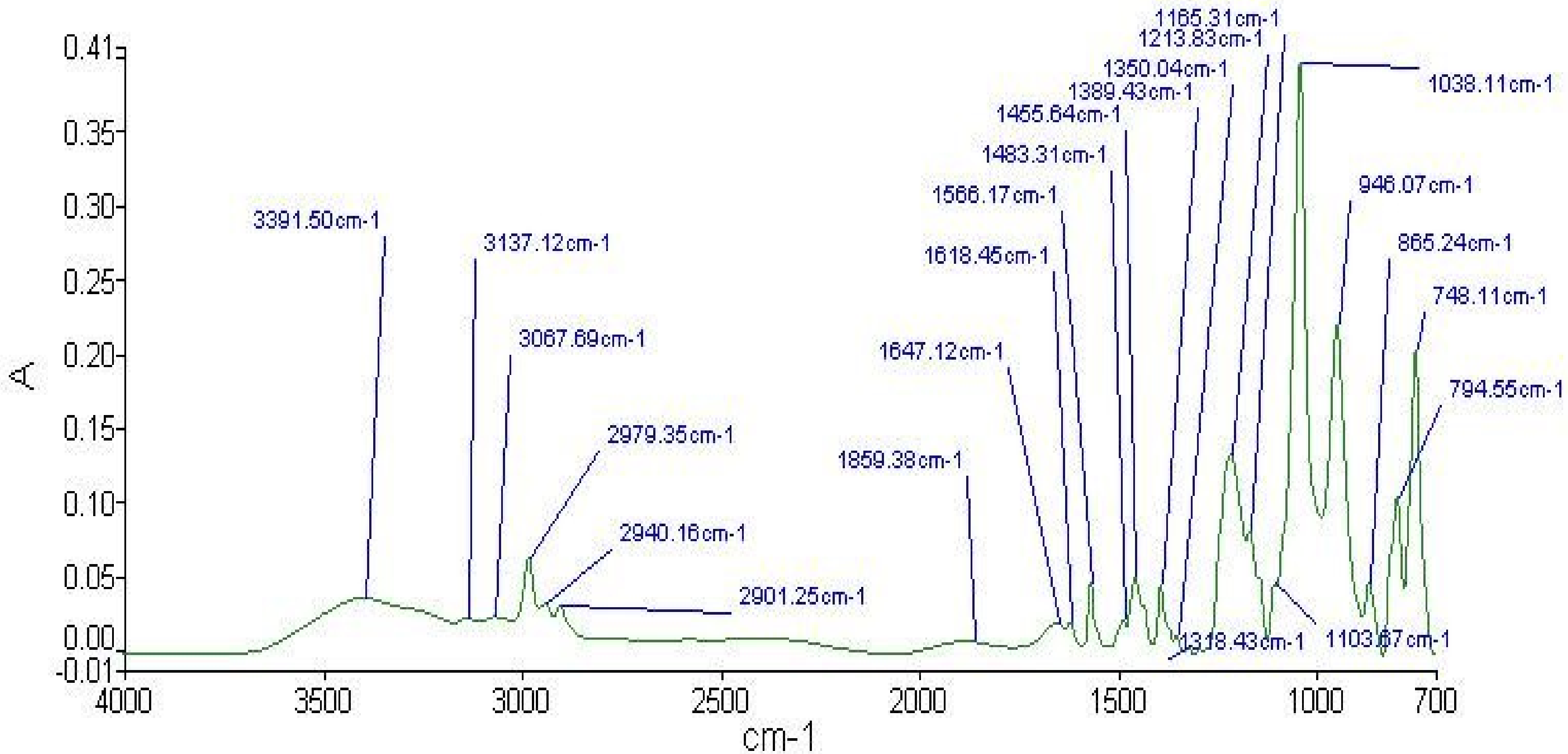

Figure 4-1: FTIR analysis result

Possible structure of 3-ethylimidazalium-ethyl phosphate

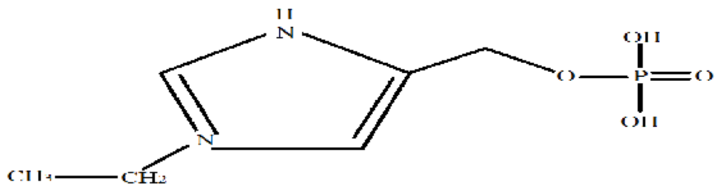

Figure 4-2: Structure of 3-ethylimidazalium-ethyl phosphate

Table 4-1: Analysis of FTIR spectroscopy result

Peak number	Wavenumber (cm^{-1})	Functional group	Molecular motion
1	748.11	aromatics	C-H bends (ortho)
2	794.55	amines	N-H bends
4	946.07	anhydrides	C-O stretch
6	1103.67	ketones	C-C stretch
7	1165.31	phosphine oxides	P=O
9	1318.43	amines	C-N stretch (aryl)
23	3391.5	alcohols	O-H

From the Table 4-1 analysis,it is know that from possible structure of 3-ethylimidazalium-ethyl phosphate, this ionic liquid contain at wavelength 748.11cm^{-1} its refer to C-H bend (ortho) from aromatics group, at wavelength 794.55cm^{-1} its refer to N-H bend from amines group, at wavelength 946.07cm^{-1} its refer to C-O stretch from anhydrides group, at wavelength 1103.67cm^{-1} its refer to C-C stretch from ketones group, at wavelength 1165.31cm^{-1} its refer to P=O from phosphine oxides group, at wavelength 1318.43cm^{-1} its refer to C-N stretch (aryl) from amines group, and at wavelength 3391.5 its refer to O-H stretch from alcohols group.

4.3 Summary

Result of FTIR analysis show the graph of different wavelength for different element. Its analyze the element wavelength in range of $700cm^{-1}$ to $4000cm^{-1}$. It is know that from possible structure of 3-ethylimidazalium-ethyl phosphate, this ionic liquid contain at wavelength $748.11cm^{-1}$ its refer to C-H bend (ortho) from aromatics group, at wavelength $794.55cm^{-1}$ its refer to N-H bend from amines group, at wavelength $946.07cm^{-1}$ its refer to C-O stretch from anhydrides group, at wavelength $1103.67cm^{-1}$ its refer to C-C stretch from ketones group, at wavelength $1165.31cm^{-1}$ its refer to P=O from phosphine oxides group, at wavelength $1318.43cm^{-1}$ its refer to C-N stretch (aryl) from amines group, and at wavelength 3391.5 its refer to O-H stretch from alcohols group.

5.0 CONCLUSION

5.1 Conclusion

3-ethylimidazalium-ethyl phosphate, this ionic liquid contain at wavelength 748.11cm^{-1} its refer to C-H bend (ortho) from aromatics group, at wavelength 794.55cm^{-1} its refer to N-H bend from amines group, at wavelength 946.07cm^{-1} its refer to C-O stretch from anhydrides group, at wavelength 1103.67cm^{-1} its refer to C-C stretch from ketones group, at wavelength 1165.31cm^{-1} its refer to P=O from phosphine oxides group, at wavelength 1318.43cm^{-1} its refer to C-N stretch (aryl) from amines group, and at wavelength 3391.5 its refer to O-H stretch from alcohols group.

5.2 Future Work

The volume of Ionic Liquid prepared should excess in volume so that experiment can be repeat more than two times if theres an error in the first experiment. The optimal absorption and desorption temperature are 298 K and 363 K, respectively. Make sure the temperature while using magnetic stirrer is constant at 323 K. Make sure the tube flow is good to avoid the ionic liquid absorb only little NO_2 in fuel. Ionic liquid must be dry for 2 days at 323 K to get the good ionic liquid solution mixture.